

# Advanced setup for high-pressure and low-temperature neutron diffraction at hydrostatic conditions

Konstantin A. Lokshin<sup>a)</sup> and Yusheng Zhao

LANSCE-12, Los Alamos National Laboratory, Los Alamos, New Mexico 87544

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We describe a design of the experimental setup for neutron diffraction studies at low temperatures and hydrostatic pressure. The significant benefit of the setup, compared to the previous methods, is that it makes possible the simultaneous collection of neutrons diffracted at the 30°–150° range with no contamination by the primary scattering from the sample surroundings and without cutting out the incident and diffracted beams. The suggested design is most useful for third-generation time-of-flight diffractometers and constant wavelength instruments. Application of the setup expands the capabilities of high-pressure neutron diffraction, allowing time-resolved kinetics and structural studies, multihistogram Rietveld, and pair distribution function and texture analyses. The high efficiency of the setup was proven for the HIPPO diffractometer at Los Alamos Neutron Science Center under pressures up to 10 kbar and temperatures from 4 to 300 K. © 2005 American Institute of Physics. [DOI: 10.1063/1.1928448]

## I. INTRODUCTION

Neutron diffraction under high pressure is a powerful method of characterizing structures. It was first implemented in the 1960s with the use of a piston-cylinder apparatuses that produce up to ~30 kbar pressure.<sup>1–3</sup> During the last decades this method has been significantly developed to satisfy different experimental requirements, i.e., pressure and temperature ranges, pressure gradients, exposure time, and others. At present, the commonly used pressure cells for neutron diffraction fall into three major categories: hydrostatic (including gas and liquid) cells,<sup>4–11</sup> large size (sample volume 10–1000 cm<sup>3</sup>) anvil cells,<sup>12–15</sup> and diamond (or sapphire) anvil cells (DACs) (sample volume 0.0001–5 mm<sup>3</sup>).<sup>16–19</sup> The last of these three techniques produces record pressures of about 1 Mbar, but only when the sample size is small. However, the currently available neutron sources do not provide sufficient flux to study samples of less than ~1 mm<sup>3</sup>, making the wide implementation of this technique for neutron diffraction studies difficult. The development of anvil cells, including those with toroid and different multianvil chambers, has allowed the limitation of the pressure of the piston-cylinder apparatuses to be overcome. Toroid anvils are used for neutron diffraction at pressure of up to ~200 kbar but usually cause a sample texture, which diminishes the quality of the data for structural refinements.

The neutron diffraction in combination with the hydrostatic (gas, liquid, or fluid) pressure has two different approaches: one using different designs of piston-cylinder apparatuses<sup>4–6</sup> and the other using indirectly pressurized cells.<sup>7–11</sup> Both techniques are limited to ~30 kbar pressure only. Nevertheless, the hydrostatic pressure neutron diffraction has become very popular and is a powerful means of

characterizing samples because of the advantages this technique offers in comparison with the other two methods. First, it allows a hydrostatic pressure medium to be used including the best available helium gas/fluid. This assures the absence of pressure gradients on the sample and the absence of stress-induced texture. It also allows pressure to be measured precisely. Large sample volume, up to 15 cm<sup>3</sup>, is another important advantage of this method for neutron studies.<sup>4,7</sup> The moderate weight and dimensions of gas pressure cells and their relatively simple adjustment for neutron diffraction experiments encourages the broad application of this technique for high-pressure, low-temperatures experiments.

Hydrostatic pressure neutron diffraction is typically used for determining crystal or magnetic structure of a sample and finding its phase transformations. This technique has also been used for kinetics studies of slow chemical reactions under high pressure with a data-collection time step of 10–30 min.<sup>20–22</sup> It should be noted that the capability of this method is usually limited by the characteristics of the diffractometer, which have been significantly improved over the last decades. Our experimental setup design considerably expands the applicability of hydrostatic high-pressure neutron diffraction and could be used for other neutron-scattering experiments.

## II. RESULTS AND DISCUSSION

### A. Previous designs

The majority of neutron diffractometers are built in so-called plane geometry, i.e., the incident beam, the sample, and the detectors are placed in the same plane. The instruments usually have a vertically elongated barlike beam cross-section designed to maximize the beam's intensity without loss of resolution. At the same time, due to the specifics of the method, the hydrostatic pressure cells are fashioned in a cylinder shape with a small cylindrical opening

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: lokshin@lanl.gov

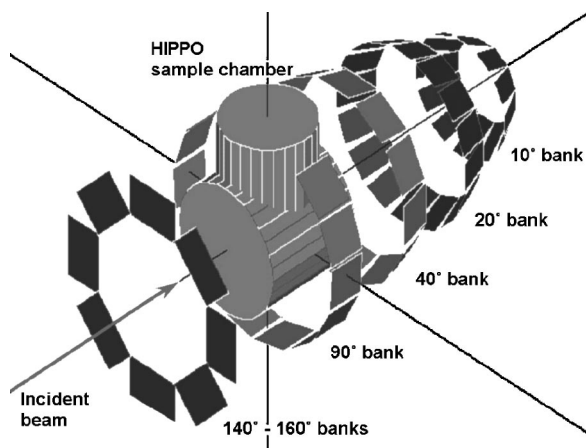


FIG. 1. Detector geometry of the HIPPO diffractometer at LANSCE.

inside. Cells are typically made from hard materials, which have low attenuation for neutrons (Al, Cu/Be, Ti/Zr alloys). The properties of the materials together with the cell design and the ratio of the outer to the inner diameters define the maximum pressure rating of a cell. It should be noticed that manufacturing the high rated pressure cell is much easier when its inner diameter is rather small (5–10 mm).

Taking into account low neutron beam flux and the beam's barlike cross section, the high-pressure cell is usually placed vertically in the diffractometers to allow maximum sample exposure. However, while this geometry optimizes the exposure of the sample volume in the beam, it causes an annoying scattering from the sample surroundings, i.e., high-pressure cell, sample holder, etc.<sup>8,11</sup> The diffraction data contaminated with the parasitic scattering from the sample environment significantly diminish the quality of the crystal structure refinements.

One of the solutions for this problem is to use a zero-scattering Ti/Zr alloy cell.<sup>10</sup> This approach is very convenient for various types of experiments, but fails for those that require special gas mediums, such as hydrogen, nitrogen, oxygen, and others. A rather high absorption of the Ti/Zr alloy is another disadvantage, which does not allow fast data collection for time-resolved studies.

The scattering from the environment may be also be eliminated by shielding the incident and the diffracted beams, but only at the cost of a substantial reduction in collected intensity. For the most favorable case of 90° data collection, the intensity decreases about two times if all primary scattering from the cell is eliminated.<sup>9</sup> Much more signal-intensity loss occurs as the scattering angle differs from 90°.

## B. New concept of the setup for neutron diffraction at hydrostatic pressure

Progress in instrument development during the last decades has resulted in the appearance of third generation diffractometers built in nonplanar geometries. For example, HIPPO at LANSCE and GEM at ISIS, both time-of-flight (TOF) instruments, have circular beam cross-sections, and detectors covering more than  $2\pi$  steradians in a solid angle. The diffractometer geometry and the detector arrangement in HIPPO are shown in Fig. 1. Obviously, the previously used

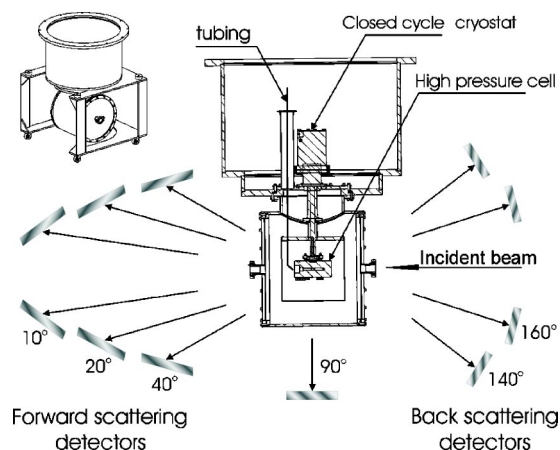


FIG. 2. Schematic general view (in the top left corner) and the enlarged section view of the setup designed for high hydrostatic pressure and low-temperature neutron diffraction experiments at HIPPO diffractometer.

design of the high-pressure cell arrangement is inefficient for these types of diffractometers. To improve the situation, we designed a new setup, which takes advantage of three-dimensional diffractometer geometry. Our setup has been successfully tested in low-temperature, high-pressure neutron diffraction experiments.

Schematic general and section views of the setup are shown in Fig. 2. The high-pressure cell is attached to the closed-cycle cryostat and surrounded by two temperature shields, allowing it to cool down to 4 K. The cryostat stands on the diffractometer cover, which can be moved and used off-line for testing and preparation procedures. The cell pressurizes indirectly via thin high-pressure tubing coming through a standard vacuum connector.

The significant difference of this design in contrast to previous experimental setups (with vertically arranged cells) is the horizontal cell alignment, in which the incident beam comes from the buttend of the cell. This cell arrangement allows experimenters to choose the position of the sample along the cell and to adjust it to the most favorable detector geometry. Placing the sample in the middle of the cell results in its separation from the cell walls (along the incident beam direction) by a rather long distance, about 2–4 cm. This separation permits shielding the system, which absorbs all the primary scattering from the cell but allows most of the diffracted beams from the sample to pass through.

The schematic illustration of the cell-shielding system is presented in Fig. 3. The plug of the cell (3) is equipped with the disk (2) made from absorbing materials (Gd, Cd, BN, etc). Thus, the buttend of the cell is the only environmental part producing Bragg scattering. This parasitic scattering can be easily blocked with the shielding system, as shown in Fig. 3. It should be noted that this example simply demonstrates in general how impurity scattering may be shielded. A precise calculation is required for each particular system, taking into consideration cell dimensions and the position of the sample and the detectors. The main advantage of this setup design is that for third generation diffractometers both the incident and the diffracted beams are not cut, and the sample data can be collected in a wide scattering angle range without contamination by impurity Bragg scattering from the envi-

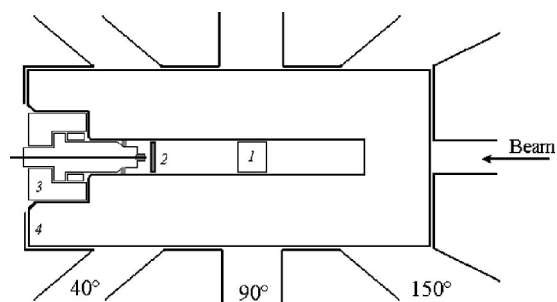


FIG. 3. Section view of the horizontally aligned high-pressure cell and the shielding system (shown by the solid lines surrounding the cell): (1) sample position; (2) Gd or Cd disk; (3) plug for the cell; and (4) high-pressure cell body.

ronment. However, as applied to instruments built in the plane geometry, the proposed design may result in significant cutting of the incident beam and reducing of the sample size from what it would be with the vertical configuration.

The application of this setup design may expand the capabilities of high-pressure neutron diffraction. First, simultaneous collection of pure diffraction data at all different data banks allows experimenters to perform high quality, single-phase Rietveld and pair distribution function analysis to determine a structure's characteristics. It should be noted that this advantage is valid for both TOF and constant wavelength instruments. Second, a multihistogram Rietveld refinement of the TOF diffraction data in the wide-angle range ( $30^\circ$ – $150^\circ$ ) can give reliable texture parameters together with structural data. Third, when applied to high intensity instruments, this setup may be used for time-resolved studies.

### C. Hydrostatic pressure setup at LANSCE

We developed the high-pressure and low-temperature setup for the HIPPO diffractometer at LANSCE based on our design. The HIPPO instrument is configured to provide an extremely high neutron flux ( $\sim 10^7$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ ).<sup>23</sup> We used a specially prepared multilayer autofretted aluminum-alloy cell to minimize neutron absorption by the cell. These advantages, together with the large sample volume (up to  $10 \text{ cm}^3$ ) of the gas cell, make this setup suitable for a variety of applications including structure analysis, texture measurements, and kinetics studies. Our setup was successfully tested at 4–300 K and 1–10,000 bar of He pressure.

The efficiency of the setup was proven in our *in situ* high-pressure, low-temperature neutron diffraction experiments on the crystal structure and formation kinetics of ice phases and of clathrate hydrates.<sup>24–26</sup> Figure 4 shows an example of the diffraction pattern of ice II obtained under 3 kbar at 215 K for 5 min with no impurity peaks from the environment. This experiment demonstrates the applicability of our setup for time-resolved structure and kinetic studies within a very short time step of 2–5 min. These 5 min diffraction patterns obtained simultaneously at  $40^\circ$ ,  $90^\circ$ , and  $150^\circ$  data banks were successfully refined by the Rietveld method. The ice II phase was refined in the *R*-3 space group with unit cell parameters  $a=12.9478(4) \text{ \AA}$  and  $c=6.2114(2) \text{ \AA}$ .

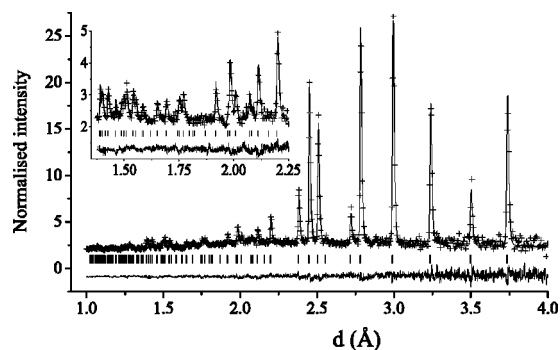


FIG. 4. Rietveld refinement pattern of the neutron diffraction data obtained at  $90^\circ$  scattering bank for Ice II under 3 kbar at 215 K for 5 min. The observed intensities are represented by plus signs (every fourth point is shown), the calculated pattern—by solid line, allowed Bragg positions—by short vertical bars, and the difference curve is shown below. A part of the high-resolution diffraction data refinement collected at  $150^\circ$  bank is shown in the inset.

It should be mentioned that in a TOF experiment, precision of the lattice constant measurements depends on the ability to maintain the sample position with high accuracy. Controlling the sample position is more difficult for the suggested setup design than for the designs with a vertical cell arrangement. For our setup, assuming a 10 m flight path length of HIPPO, backscattering data collection (at  $180^\circ$ ), and an ability to maintain the sample position within 0.1 mm at  $p < 10$  kbar, the maximum error in the unit cell parameter caused by the uncertainty in the sample position is estimated as  $2 \times 10^{-5}$ . The value of this quantity is usually below the standard deviation of the lattice constants determined from the Rietveld refinement (for instance, the error in the ice II refinement shown above for  $\epsilon_a=0.00026$  and  $\epsilon_c=0.00012$ ). However, in the experiments aimed at precise measurement of unit cell parameters, such as compressibility measurements, the problem of controlling the sample position may affect the quality of obtained data.

Finally, the suggested design could be used for other types of neutron scattering experiments under high pressure, including measurements of inelastic scattering, reflectometry, and vibrational spectroscopy.

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<sup>1</sup>D. F. Litvin and E. G. Ponyatovskii, *Kristallografiya* **11**, 354 (1966) [*Springer Proc. Phys.* **11**, 322 (1966)].

<sup>2</sup>R. M. Brugger, R. B. Bennion, and T. G. Worlton, *Phys. Lett. A* **24**, 714 (1967).

<sup>3</sup>R. M. Brugger, R. B. Bennion, T. G. Worlton, and W. R. Myers, *Trans. Am. Crystallogr. Assoc.* **5**, 141 (1969).

<sup>4</sup>A. S. Vindryavskiy, S. N. Ishnaev, I. P. Sadicov, and A. A. Chernyshov, *Phys. Lett. A* **76**, 355 (1980).

<sup>5</sup>R. Millet and R. J. Papoular, *Rev. Phys. Appl.* **19**, 827 (1984).

<sup>6</sup>A. N. Ivanov, D. F. Litvin, B. N. Svenko, L. S. Smirnov, V. I. Voronin, and A. E. Teplykh, *High Press. Res.* **14**, 209 (1995).

- <sup>7</sup>R. Lechner, *Rev. Sci. Instrum.* **37**, 1534 (1966).
- <sup>8</sup>W. F. Kuhs, B. Chazallon, P. G. Radaelli, and F. Pauer, *J. Inclusion Phenom. Mol. Recognit. Chem.* **29**, 65 (1997).
- <sup>9</sup>J. D. Jorgensen, S. Pei, P. Lightfoot, D. G. Hinks, B. W. Veal, B. Dabrowski, A. P. Paulikas, R. Kleb, and I. D. Brown, *Physica C* **171**, 93 (1990).
- <sup>10</sup>O. Yamamuro, K. Okishiro, T. Matsuo, T. Ohta, Y. Kume, and R. M. Ibberson, *Physica B* **241–243**, 466 (1997).
- <sup>11</sup>F. K. Katsaros, T. A. Steriotis, K. L. Stefanopoulos, N. K. Kanellopoulos, A. Ch. Mitropoulos, M. Meissner, and A. Hoser, *Physica B* **276–278**, 901 (2000).
- <sup>12</sup>J. M. Besson, R. J. Nelmes, G. Hamel, J. S. Loveday, G. Weill, and S. Hull, *Physica B* **180–181**, 907 (1992).
- <sup>13</sup>S. Klotz, M. Gauthier, J. M. Besson, G. Hamel, R. J. Nelmes, J. S. Loveday, R. M. Wilson, and W. G. Marshall, *Appl. Phys. Lett.* **67**, 1188 (1995).
- <sup>14</sup>A. N. Ivanov, D. F. Litvin, N. V. Pashkin, B. N. Svenko, L. S. Smirnov, and Yu. V. Taran, *High Press. Res.* **14**, 203 (1995).
- <sup>15</sup>Y. Zhao, R. B. Von Dreele, and J. G. Morgan, *High Press. Res.* **16**, 161 (1999).
- <sup>16</sup>S. Sh. Shi'shtein, V. P. Glazkov, I. N. Makarenko, V. A. Somenkov, and S. M. Stishov, *Fiz. Tverd. Tela (Leningrad)* **25**, 330 (1983).
- <sup>17</sup>V. P. Glazkov, S. P. Besedin, I. N. Goncharenko, A. V. Irodova, I. N. Makarenko, V. A. Somenkov, S. M. Stishov, and S. Sh. Shil'shtein, *Pis'ma Zh. Eksp. Teor. Fiz. [JETP Lett.]* **47**, 661 (1988).
- <sup>18</sup>V. P. Glazkov, A. V. Irodova, V. A. Somenkov, S. Sh. Shil'shtein, and S. P. Besedin, *J. Less-Common Met.* **129**, 165 (1987).
- <sup>19</sup>J. Xu *et al.*, *High Press. Res.* **24**, 247 (2004).
- <sup>20</sup>B. Morosin, Z. Hu, J. D. Jorgensen, S. Short, J. E. Schirber, and G. H. Kwei, *Phys. Rev. B* **59**, 6051 (1999).
- <sup>21</sup>R. W. Henning, A. J. Schultz, V. Thieu, and Y. Halpern, *J. Phys. Chem. A* **104**, 5066 (2000).
- <sup>22</sup>S. Bobev and K. Tait, *Am. Mineral.* **89**, 1208 (2004).
- <sup>23</sup>H.-R. Wenk, L. Lutterottia, and S. Vogel, *Nucl. Instrum. Methods Phys. Res. A* **515**, 575 (2003).
- <sup>24</sup>K. A. Lokshin, Y. Zhao, D. He, W. L. Mao, H.-K. Mao, R. J. Hemley, M. V. Lobanov, and M. Greenblatt, *Phys. Rev. Lett.* **93**, 125503 (2004).
- <sup>25</sup>K. A. Lokshin and Y. Zhao, *Appl. Phys. Lett.* (submitted).
- <sup>26</sup>K. A. Lokshin and Y. Zhao, US Patent No. 10/886,229 (8 July 2004).